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温度 "駆動" の相転移ダイナミックス
Dynamics of Temperature Driven Phase Transitions

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Abstract

我々は SF_6 分子クラスターにおける2種の固体構造（*bcc* 配位の無秩序相と歪んだ単斜配位の秩序相）の "熱的な" 共存が、TeF_6 分子クラスターに比べて、計算機実験において観測に掛りづらい原因を解析した。本稿では、遷移 "温度" 近傍のエネルギー一定の MD トラジェクトリーを継続的に conjugate gradient 法を用いて徐冷することで、$(SF_6)_{89}$ クラスターの場合（ポテンシャルエネルギー面上で鞍点を介して）相互に繋がっている極小エネルギー構造間の相対エネルギーは、完全な配位秩序相に相当する最安定エネルギー構造を除いて、ほぼ同じであること；$(SF_6)_{89}$ クラスターでは部分的に秩序を持った構造が占める相空間体積の割合が "秩序—無秩序相の共存がシュミレーションにおいて容易に達成される" $(TeF_6)_{89}$ クラスターに比べて小さいこと；SF_6 と TeF_6 分子は同じ対称性を持ち、かつ同じ原子間相互作用ポテンシャル関数で記述されているが、ポテンシャルエネルギー面の topography は、「系のダイナミックスを大きく左右する」局所安定点—鞍点—（別の）局所安定点（minimum-saddle-minimum）のエネルギー比において、顕著に異なっており、この違いが「TeF_6 は（SF_6 に比べて）部分秩序相により長く滞在し、共存相が観測される温度領域において高いエネルギーの局所安定点群と部分秩序相を有意に分離させている」原因となっていること、を示す。

We have investigated why the thermal coexistence of two solid structures (*bcc* orientation disordered phase and strained monoclinic orientation ordered phase) is more difficult to be observed in computer simulations of SF_6 molecule clusters than of TeF_6 molecule clusters. By successive conjugate gradient quenching of constant energy MD trajectories in the vicinity of transition temperatures we show that in the case of $(SF_6)_{89}$ cluster the relative energies of the most linked minima differ only a little. An exception is the global minimum related to a complete orientation ordered phase. At relevant temperatures, the fraction of the available phase space of the $(SF_6)_{89}$ cluster corresponding to a partially-ordered structure is smaller than it is for the $(TeF_6)_{89}$ cluster. The latter readily exhibits coexistence of the ordered and disordered forms, in simulations. Although the SF_6 and TeF_6 molecules have the same symmetry and we use the same form of interatomic interaction potentials to describe their clusters the topographies of the potential energy surfaces differ significantly in the values of minimum-saddle-minimum ratios that determine the system dynamics. This results in better separation of the higher-energy local minima of the TeF_6 cluster, and longer residence times in the partially-ordered form, in the temperature range of coexistence.

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I. INTRODUCTION

Cluster phase transformations form a multi-faceted field of study, involving the untangling of many-body physics spanning wide ranges of length- and time-scales and describing thermal effects in phase spaces with complex topographies. It has long been known that small clusters of various sizes can exhibit different phase-like forms that may coexist [1]. In a small system one or more linear dimensions are of order of the interaction characteristic length. This affects the properties of the small systems that can be rather different from those of their bulk counterparts. For example, the coexistence of two or more phase-like forms in finite systems can be observed over *ranges* of temperatures, not just along curves, e.g. as given by $p_{vap}(T)$, as it is in bulk. More commonly, one might observe dynamical coexistence of solid and liquid clusters together in an ensemble [2]. Another example is the coexistence of two solid-like forms with different structural symmetries [3]. We should be aware that in the case of molecules, just classifying the states of the condensed matter as either solid or liquid may be too simplistic since quenching of a liquid can yield amorphous or glassy structures, or partially- or completely-ordered solids [4]. The peculiarities of the molecular systems are caused by their rugged potential energy surface, which traps the system in one of its innumerous local minima corresponding to various structures [5,6]. That is why it is quite difficult to freeze the system into a one single crystal structure corresponding to the global minimum.

The variety of structures originates from the orientation dependence of the intermolecular potential. Due to that anisotropy, the transition between the different structures involves both lattice reconstructions and orientation

ordering, achieved by molecular rotation, which may actually and strictly be libration. The vibration and rotation often couple to each other, which makes impossible the decomposition of the molecular spectra into purely rotational and vibrational bands. On the other hand, this coupling can be of certain use in the study of continuous phase transitions, by setting restrictions on the possible lattice symmetries of the cluster structures [7]. No massive ionic displacements occur when such coupling happens and the basic arrangement of the ions is essentially unchanged, thus giving rise to a continuous transition to the new phase.

The coexistence of two phases is observable if a cluster spends time intervals long enough to establish characteristic equilibrium properties in each phase. The question of how to describe the equilibrium between two phases has been discussed in the cluster physics literature [1]. The coexistence of two cluster forms is a consequence of their local stability expressed via $d^2S < 0$ where $S(E,N)$ is the entropy of the system; i.e. the entropy of a stable form is a *concave* function of its variables - the total energy E of the N-particle system. The phase transitions between two (or more) forms can be classified through the curvature determinant $D(E,N) = \partial^2 S/\partial E^2 * \partial^2 S/\partial N^2 - (\partial^2 S/\partial E \partial N)^2$: $D < 0$ corresponds to a first-order phase transition, $D = 0$ characterizes a continuous transition, and $D > 0$ denotes a stable form. In other words, the topography of $S(E,N)$ determines the behavior of the system when an external field (thermal, electric, magnetic) is applied.

In this research we show how the rich variety of complex phenomena in condensed matter arises from the well-understood, simple underlying interactions among ingredients. The specific question to which we seek a partial answer here is: To what extent is the kind of transition (continuous or discontinuous) determined by the underlying space symmetry of the potential of interaction or by the set of values of the parameters of the potential?

II. TOOL FINITE-SYSTEMS AND THEIR HAMILTONIANS

Clusters of chalcogen hexafluorides, SF_6 and TeF_6, have been studied for more than two-decades both experimentally and theoretically. A common experimental device to produce such clusters is the supersonic jet [8,9]. In computer simulations of these systems, the molecules of SF_6 and TeF_6 are treated as rigid octahedra with S or Te in the centers and F atoms located at constant bond lengths from them. A small negative charge (less than $0.5e$) is associated with the F atoms that gives rise to Coulomb interactions. The orientation dependence of the interatomic potential is described via a sum over atom-atom pair-wise $U_{pw(i,j,\alpha,\beta)}$ potentials:

$$U_{pot} = \sum_{i,j=1\,(i<j)}^{n} U_{pw(i,j)}(\sigma_{\alpha\beta}, \epsilon_{\alpha\beta}) \tag{1}$$

where r_{ij} is the distance between the i-th and the j-th atom. The indices α and β denote either a fluorine or a tellurium (sulphur) atom. The values for $\sigma_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$ are given elsewhere [4]. The Hamiltonian equations of motion with the given potential have been calculated in a constant energy ensemble with the help of the velocity Verlet algorithm. The integration time step has been determined to be 5 fs, which preserves the energy up to 10^{-6} far away from the transition region and 10^{-4} in its vicinity.

Despite the similarity of the SF_6 and TeF_6 molecules, the simulated thermal behavior of clusters of SF_6 and TeF_6 has been reported to be different in Ref. [10,12], namely they exhibit different structures and different kinds of transitions on cooling/heating. The transitions in TeF_6 clusters have been recognized as continuous [10], while those in SF_6 - as discontinuous, [12]. In the latter case however, no evidence for coexistence of liquid and solid forms has been found [13], although it should be observed if the transition is of first order.

It is very instructive to investigate the origin of the differences in thermal behavior of free SF_6 and TeF_6 clusters. We have undertaken a theoretical comparative study of those substances to shed light on the subject. This phenomenon is related to understanding how to control the transitions between the variety of a cluster's forms, which has both fundamental and technological importance. In order to investigate the role of the potential symmetry and the parametric manifold in the phase transformations of molecular clusters we analyze the perturbative role of the time-space discretization on the trajectories of classical Hamiltonian systems [14].

The initial Hamiltonian $H(\overrightarrow{p}, \overrightarrow{q})$ is integrable and satisfies the requirement of having n-independent constants of motion f_i. The last implies that the trajectory of the system in phase space is restricted to lie on an n-dimensional surface: $f_i(\overrightarrow{p}, \overrightarrow{q}) = k_i$; $i = 1, ..., n$, where the k_i are constants.

For constants of motion f_i, the Poisson bracket is $\{f_i, H\} = 0$, and it is known that $\{f_i, f_j\} = 0$ for each $i, j = 1, ..., n$. This restricts the topology of the surface, $f_i(\overrightarrow{p}, \overrightarrow{q}) = k_i$, to be of certain type: it must be an n-dimensional torus. Thus for integrable systems, the phase space is completely occupied by n-tori, almost all of which are filled by n-frequency quasi-periodic orbits. In contrast with the case of n frequency quasi-periodicity is the case of true periodic motion, in which orbits on the n-torus close on themselves. Thus, arbitrarily near any torus on which there is n-frequency quasi-periodicity, there are tori on which the orbits are periodic. On a complex PES, the trajectories wander

and a small random perturbation, caused for example by truncation error, might lead the system to one or another set of tori, possibly far distant from the first.

We study temperature-driven phase transitions of a Hamiltonian system and specially, dynamical coexistence of phase-like forms. In order to observe such phenomena, we should follow the trajectory $(\overrightarrow{p}, \overrightarrow{q})$ for a time t long enough for the system to exhibit oscillations and diffusion characteristic of a specific phase, so that we should choose $t \sim 100 \sum_i \tau_i$, where τ_i is a characteristic time of the i-th phase. Here we meet the competing sources of errors: Δt and the truncation error limited by the number of digits carried by our digital computer. If we decrease Δt, then the computational time increases and inaccuracy due to the accumulated error increases. The choice of Δt can be optimized of course but at any instant, the truncation acts as a small perturbation γ, which effectively changes the Hamiltonian $H'(\overrightarrow{p}, \overrightarrow{q})$:

$$H'(\overrightarrow{p}, \overrightarrow{q}) = H(\overrightarrow{p}, \overrightarrow{q}) + \gamma H_1(\overrightarrow{p}, \overrightarrow{q}).$$

Then we should expect that for a typical form of perturbation, $H_1(\overrightarrow{p}, \overrightarrow{q})$, all the constants of motion for the integrable system, $H'(\overrightarrow{p}, \overrightarrow{q})$, except the constant energy, $E = H'(\overrightarrow{p}, \overrightarrow{q})$, are immediately spoiled as soon as $\gamma \neq 0$. For small γ, orbits would initially approximate the orbits of integrable system, staying close to unperturbed n-tori that exist for $\gamma = 0$ for at least short times.

What do we gain from this analysis? First, it gives us a way to relate the results of different computations to the lengths of the computational times and the truncation errors that induce a perturbation H_1 in the initial Hamiltonian. This in turn might bring the system to a temporary periodic orbit. In such a case the system spends some time in a restricted region of the phase space, which acts temporarily as if it were an attractor. Excepting the total energy, the studied quantities have different values when averaged over a trajectory with or without "attractors".

Second, the analysis explains why, in some simulations, people do not detect phase coexistence: to observe this, the trajectory must visit the phases several times during the run and should stay in each long enough (at least tens of characteristic times) in order to obtain a proper averaging of the fluctuating quantities (the kinetic and the potential energy).

III. RESULTS AND CONCLUSION

In order to compare the $(TeF_6)_{89}$ and $(SF_6)_{89}$ dynamics in the vicinity of solid-solid phase transitions, we have quenched the Molecular Dynamics trajectory and have obtained the coexistence structures. Quenching is a means to associate arbitrary points in the phase space with the local minima in whose wells they lie on the PES [15]. We have used the conjugate gradient method to minimize the energy of the MD trajectory. At the end of every 250 *fs* interval, we have recorded the quenched structures and have subsequently performed normal mode analysis.

The Fig.1 indicates two well-resolved states after quenching, with total binding energies of (-18.4 eV) and (-19.2 eV). The structures corresponding to these energies are orientationally-disordered cubic and partially ordered monoclinic. The evolution of the cluster, seen in animations [16], shows that the orientation ordering transformations are initiated at the surface. The evolution of the SF_6 cluster, Fig.2, indicates that the potential energy surface has another topography determined by the parametric manifold for the case of kept spatial symmetry of the Hamiltonian.

The detailed analysis of the topography of PES reveals the reason for the phases of the SF_6 clusters being less distinguishable than those of the TeF_6 cluster: the smoother landscape of the sulfur PES increases the rate constants for transitions between neighboring minima. This decreases the time the system spends in a specific phase. Because of that, one should perform very long runs, with a carefully selected step of integration Δt and with enough slightly different initial points in the phase space in order to avoid quasi-periodic orbits generated by truncation of the numbers in the computers.

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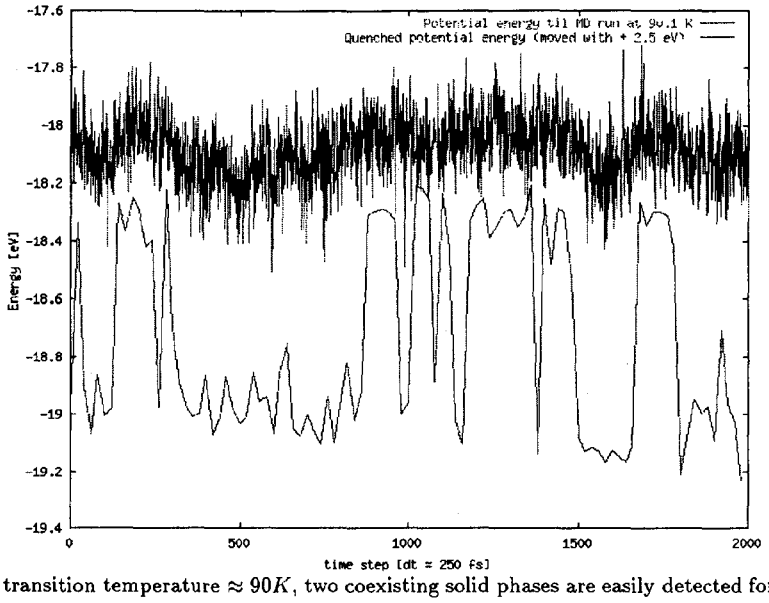
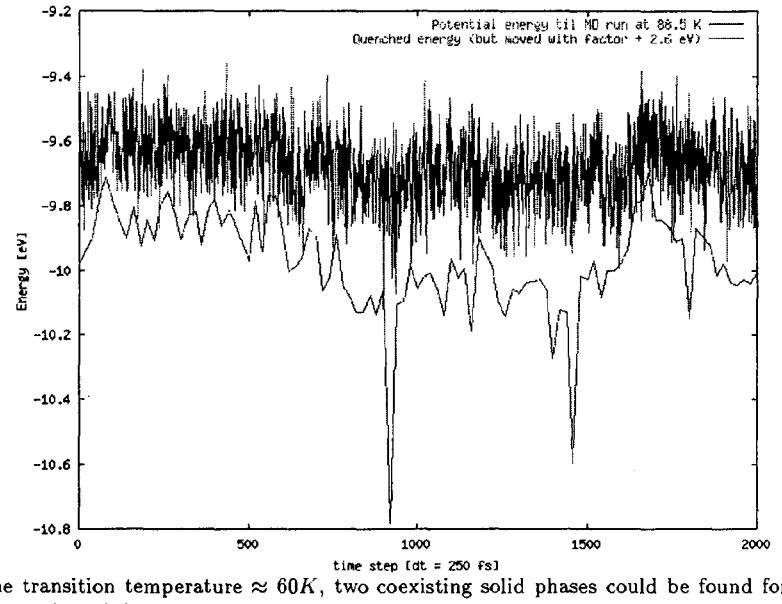


1em FIG. 1. At the transition temperature $\approx 90K$, two coexisting solid phases are easily detected for the 89-molecule TeF_6 cluster.



1em FIG. 2. At the transition temperature $\approx 60K$, two coexisting solid phases could be found for the 89-molecule SF_6 cluster after a proper spanning of the space phase.